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Cooling processes for a 1D structural 'glass' model

Walter Kob† and Rolf Schilling‡

Institute of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland

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Abstract. The dependence of the residual energy e_{res} on the cooling rate γ is investigated numerically for a one-dimensional chain of classical particles with anharmonic competing interactions. Due to the complex landscape of the potential energy of the system, with exponentially many barriers and valleys, $e_{res}(\gamma)$ shows a non-trivial behaviour. For large cooling rates e_{res} is independent of γ. In the intermediate γ-range some plateaux are found which can be understood by means of a simple double well potential and for small γ we find a power-law behaviour for $e_{res}(\gamma)$, which supports a conjecture by Grest *et al.* This power-law behaviour can be explained analytically by means of a kinetic Ising model and the correspondence of the exponents from the analytical theory and those from the simulation is fair for a certain range of the potential parameters.

1. Introduction

Experience shows that most materials become crystalline when cooled from the liquid phase sufficiently slowly. For cooling rates higher than a certain (material-dependent) value the final state will be an amorphous solid. Thus, concerning the phenomena of glass transition and the formation of order from disorder, the cooling rate dependence of the solidification process is of primary interest.

To our knowledge only a few works have discussed this question up to now. Ritland [1] found experimentally that the glass transition point T_g depends logarithmically on the cooling rate γ, a behaviour also found theoretically for several models [2, 3]. Although some experimental work has been done on investigating the final structure of various materials as a function of the cooling rate [4] no quantitative conclusions can be drawn to date.

Theoretically also, rather simple quantities related to structural properties such as, for example, the residual energy $e_{res}(\gamma)$ or the residual entropy $s_{res}(\gamma)$, are of interest. These quantities are defined as follows. Consider a system of N classical particles with potential energy $V(\{\boldsymbol{x}_j\})$ ($\boldsymbol{x}_j$ is the position of the jth particle) where $V(\{\boldsymbol{x}_j\})$ has *no extrinsic* built-in disorder. The ground state of such a system is believed to be periodic and usually $V(\{\boldsymbol{x}_j\})$ has several metastable configurations $\{\boldsymbol{x}_j^{(0)}\}$ and for glassy systems there may be even *exponentially* many. If the system is cooled from its liquid

† Present address: Department of Chemistry, Stanford University, Stanford, CA 94305, USA.
‡ Present address: Institute of Physics, University of Mainz, Staudinger Weg 7, D-6500 Mainz, Federal Republic of Germany.

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phase to zero temperature it will relax to one of these metastable configurations and the final state will depend on the cooling rate. Then the residual energy is defined as

$$e_{\mathrm{res}}(\gamma) = \lim_{N\to\infty} \frac{1}{N} [\, V(\{\boldsymbol{x}_j^{(0)}\}(\gamma)) - E_0] \tag{1}$$

where E_0 is the classical ground-state energy. Thus e_{res} (or s_{res} which is defined analogously) is a measure of the disorder present in the relaxed configuration and is expected to vanish for arbitrarily small γ.

From a mathematical point of view, finding the ground state in the presence of a huge number of metastable states is formally equivalent to a certain class of optimization problems which attracted much attention in the last few years (see, for example, the references in [5]). Much of this attraction comes from the fact that in 1983 Kirkpatrick *et al* proposed an algorithm, called simulated annealing, making such problems tractable at last [6]. Examples for this kind of optimization problems are spin glasses or the travelling salesman problem. The ground state of these problems is usually highly non-trivial, due to the extrinsic disorder, and thus generally *not* known, in contrast to the crystalline ground state of materials forming structural glasses.

To carry out simulated annealing on a computer, knowledge of the functional dependence of e_{res} on γ is crucial, since it determines the amount of computer time required to approach the ground state. Based on several examples, Grest *et al* [7] recently conjectured that for not *NP*-complete problems† this dependence can be given asymptotically (i.e. $\gamma \to 0$) by a power law

$$e_{\mathrm{res}}(\gamma) \sim \gamma^{\mu} \qquad \mu > 0. \tag{2}$$

However, a slower dependence is not ruled out, and indeed Ettelaie *et al* [9] found for $s_{\mathrm{res}}(\gamma)$ a logarithmic dependence for a 1D spin glass model (a not *NP*-complete problem). But today it is not clear whether these authors really reached in their simulation the asymptotic regime, and therefore their conclusions concerning this point might be doubtful [7]. Thus, up to now no conclusive example is known for a not *NP*-complete problem showing a logarithmic dependence of, for example, the residual energy. For *NP*-complete problems a much weaker dependence than a power law is expected, such as, for example,

$$e_{\mathrm{res}}(\gamma) \sim (-\ln \gamma)^{\zeta} \qquad \zeta > 0 \tag{3}$$

and has actually been found for various spin-glass models and the travelling salesman problem [7, 10]. Also, Morgenstern and Würtz [11] found a slow cooling rate dependence of the total wire length connecting different parts of a chip (an *NP*-complete problem), but the dependence was of a more complicated type than (3).

The conjecture by Grest *et al* was questioned by Huse and Fisher [12]. Assuming an ensemble of *independent* two-level systems with a *broad* distribution of parameters they found a *logarithmic* dependence for all dimensions, independent of whether the system is *NP*-complete or not. A similar behaviour was found by Langer *et al* for the entropy distribution of independent two-level systems [13]. After this, Freund and Grassberger [14] re-examined one of the not *NP*-complete spin-glass models

† By definition, the amount of computer time needed to solve an *NP*-complete problem grows faster than any polynomial in N, where N is the number of variables for the problem [8].

investigated previously by Grest *et al* and found their results better compatible with a logarithmic dependence. But, very recently Chakrabarti and Toral also found a power law for $e_{res}(\gamma)$ for three different not *NP*-complete spin-glass models [15].

This discussion makes it obvious that no definite result for the γ-dependence of e_{res} for systems with extrinsic disorder has yet emerged.

Recently we have calculated numerically $e_{res}(\gamma)$ for a chain of particles with competing and anharmonic interactions [16]. This model does not have any extrinsic disorder, but nevertheless some of its *static* properties resemble those of a glass [17]. Although this model (which is not *NP*-complete) does not possess a glass transition†, we expect e_{res} to depend on γ due to its complex potential energy landscape with exponentially many metastable configurations. Since the ground-state energy E_0 is known exactly for this model, we do not have to extract E_0 from the cooling data themselves to determine e_{res} from equation (1). Thus, no uncertainty is introduced at this point as is the case for most spin-glass models for which E_0 is not known exactly. Our calculations [16] showed evidence of a power law for $e_{res}(\gamma)$ with two different exponents μ for intermediate and small values of γ, respectively. For the intermediate range, this behaviour of e_{res} was thought to be explained by the freezing of a certain type of two-level systems leading to a power law, while for small γ this interpretation failed. Meanwhile numerical information obtained on a microscopic scale showed that the freezing for intermediate γ is, however, not related to the two-level systems considered originally. Since the power law, equation (2), is true only asymptotically, i.e. for $\gamma \to 0$, we have decided to extend our simulation to much smaller values of γ, which in the meantime has become possible due to better computer facilities available to us. The purpose of the present paper is to present these more elaborate results, which support the existence of an asymptotic power law, and to present an analytical calculation which corroborates our numerical findings.

For the analytical approach we take advantage of the fact that the dynamics of the chain at low temperatures can approximately be described by a kinetic Ising model. With this in mind we have recently determined $e_{res}(\gamma)$ for a one-dimensional Ising model with ferromagnetic nearest-neighbour coupling J and usual Glauber dynamics, but with an *activated* attempt frequency of the form $\alpha(T) = \alpha_0 \exp(-B/k_B T)$. An asymptotic analysis yields a power-law behaviour with exponent $\mu = \Delta/2(B+\Delta)$, where $\Delta = 4J$ is the excitation energy for a single spin flip with respect to the ferromagnetic ground state [19]. This result *cannot* be explained by the freezing of *independent* two-level systems (which would yield $\mu = \Delta/B$) but has to be interpreted as the result of diffusing domain walls separating the large domains of up and down spins which represent the relevant spin configurations at low temperatures. Unfortunately this analytical treatment of the cooling process cannot be extended to more general kinetic Ising models. Nevertheless, it will be shown below that a simplified approach, exploiting the picture of domain wall diffusion, leads to a power law for more general models too. This approach is similar to that recently used by Stinchcombe *et al* [20] for an Ising model with alternating nearest-neighbour interactions.

We will proceed as follows. The next section presents our model, the connection of its dynamics to a kinetic Ising model and the details of our simulations. In section 3 we will discuss our analytical approach leading to the power-law behaviour for the

† For finite cooling rates our model freezes at a *finite* temperature $T_f(\gamma)$. In addition, we have found a Kohlrausch law for a relaxation function. However, non-Arrhenius behaviour of the corresponding relaxation time, characteristic for most glassy systems, has not been found [18].

residual energy and compare these findings with those from the numerical simulation. A summary and conclusions are given in section 4.

2. Model and cooling procedure

The model investigated in this paper has been introduced recently to describe glass-like properties of quasi-one-dimensional materials. Here we will only sketch the main features of this model. Details can be found in [17, 18].

2.1. Static properties

We consider a chain of classical, identical particles with anharmonic on-site potential and harmonic nearest-neighbour interactions. The potential energy of the system is given by†

$$V(\{x_i\}) = \sum_i \left(\frac{C_1}{2} [(x_i - a_+ - a_-\sigma(x_i))^2 - (c - a_+ - a_-\sigma(x_i))^2] + \frac{C_2}{2}(x_i + x_{i+1} - b)^2 \right) \tag{4}$$

with x_i the displacement of the ith particle, $C_1 > 0$, and $C_2 \neq 0$. Here $\sigma(x)$ stands for $\mathrm{sgn}(x-c) \in \{\pm 1\}$ and $a_\pm$, b and c characterize the geometrical form of the potential. Thus the anharmonic on-site potential consists of two parabolae with equal second derivative C_1 patched together at $x = c$. For $a_\pm$, b and c in a certain range and $|\eta| < \frac{1}{3}$, where

$$\eta = -\kappa(1 - \sqrt{1 - \kappa^{-2}}) \qquad \text{with } \kappa = 1 + \frac{C_1}{2C_2} \tag{5}$$

it can be shown that potential (4) has exponentially many metastable configurations $\boldsymbol{x}(\boldsymbol{\sigma}) \equiv \{x_i(\boldsymbol{\sigma})\}$ which are in one-to-one correspondence with sequences $\boldsymbol{\sigma} \equiv \{\sigma_j\}$ of pseudo spins $\sigma_j = \pm 1$. For given $\boldsymbol{\sigma}$, $\boldsymbol{x}(\boldsymbol{\sigma})$ is obtained in the thermodynamic limit by

$$x_i(\boldsymbol{\sigma}) = A + B \sum_{j=-\infty}^{\infty} \eta^{|j|} \sigma_{i+j}. \tag{6}$$

Neglecting a constant term, the energy of a metastable configuration follows from the Ising-like Hamiltonian:

$$E(\boldsymbol{\sigma}) = J_0 \sum_{i \neq j} \eta^{|i-j|} \sigma_i \sigma_j - h \sum_i \sigma_i \qquad J_0 < 0. \tag{7}$$

The constants A, B, h and J_0 in (6) and (7) depend on the parameters $a_\pm$, c, b and η and can be found in [17]. In the following we always choose $C_2 < 0$, which implies $\eta > 0$.

From the above discussion it follows that for this model the *configurational* degrees of freedom, described by the Ising variables σ_i, can be separated *exactly* from the vibrational degrees of freedom. Thus changes of the configurational degrees of freedom correspond to spin flips. For transitions between two metastable configurations characterized by $\boldsymbol{\sigma}$ and $\boldsymbol{\sigma}'$, a barrier has to be overcome. The smallest of these barriers are related to *single* spin flips, i.e. to transitions between 'neighbouring' configurations. Simulations have shown that these kind of spin flips are the only relevant ones [18]. If the nth spin flips, a barrier of height

$$b_n(\boldsymbol{\sigma}) = \frac{C_1}{2} \frac{1-\eta}{1+\eta} (x_n(\boldsymbol{\sigma}) - c)^2 \geqslant B_{\min} > 0 \tag{8}$$

† The potential given by (4) is a slight modification of that considered in [17].

has to be passed ($B_{\min}$ is the minimum barrier height for single spin flips). The energy difference between both metastable configurations is

$$\Delta_n(\boldsymbol{\sigma}) = 4J_0 + 2C_1 a_- \sigma_n (x_n(\boldsymbol{\sigma}) - c). \tag{9}$$

Thus the potential energy landscape in configuration space possesses exponentially many two-level systems with an asymmetry Δ_n and barrier height b_n.

2.2. Dynamic properties

For temperatures low compared with $B_{\min}$, the system will oscillate around a metastable configuration with a microscopic frequency $\Omega \sim 10^{12}\,\mathrm{s}^{-1}$. Transitions $\{\sigma_i\} \to \{\sigma_i'\}$ will occur with a frequency which is much smaller than Ω. If in addition we assume the relaxation rate into local equilibrium to be much larger than the spin flip rate we can expect subsequent spin flips to be uncorrelated. If we denote by $p(\boldsymbol{\sigma}, t)$ the probability for having a configuration $\boldsymbol{\sigma}$ at time t, this Markov assumption leads to a master equation for $p(\boldsymbol{\sigma}, t)$:

$$\dot{p}(\boldsymbol{\sigma}, t) = -\sum_i w_i(\ldots, \sigma_i, \ldots) p(\ldots, \sigma_i, \ldots) + \sum_i w_i(\ldots, -\sigma_i, \ldots) p(\ldots, -\sigma_i, \ldots, t). \tag{10}$$

For the transition rates $w_n(\boldsymbol{\sigma})$ we will use the transition state result [21]:

$$w_n(\boldsymbol{\sigma}) = \alpha_0 \exp(-\beta b_n(\boldsymbol{\sigma})) \qquad \alpha_0 = \frac{C_1 + 4C_2}{m}. \tag{11}$$

Up to order η, this can be written as

$$\begin{aligned} w_n(\boldsymbol{\sigma}) \simeq \alpha_0 \exp\left[\beta\left(J_0 + \frac{h^2}{4J_0}\right)\right] & (\cosh \beta h - \sigma_n \sinh \beta h) \\ & \times [\cosh^2 \beta h\eta - (\sigma_{n-1} + \sigma_{n+1}) \sinh \beta h\eta \cosh \beta h\eta + \sigma_{n-1}\sigma_{n+1} \sinh^2 \beta h\eta] \\ & \times [\cosh^2 K + \sigma_{n-1}\sigma_{n+1} \sinh^2 K][1 - \tfrac{1}{2}\sigma_n(\sigma_{n-1} + \sigma_{n+1}) \tanh 2K] \end{aligned} \tag{12}$$

with $K = \beta J$ and $J = 2|J_0|\eta$. For $h = 0$ this can be further simplified to

$$w_n(\boldsymbol{\sigma}) \simeq \alpha(T)[1 + \delta(T)\sigma_{n-1}\sigma_{n+1}][1 - \tfrac{1}{2}\sigma_n(\sigma_{n-1} + \sigma_{n+1}) \tanh 2K] \tag{13}$$

where

$$\alpha(T) = \alpha_0 \exp(-\beta|J_0|) \cosh^2 K \qquad \delta(T) = \tanh^2 K. \tag{14}$$

Equation (13) represents the most general Glauber dynamics for a one-dimensional Ising model with nearest-neighbour coupling J, field $h = 0$, and fulfilling the condition of detailed balance [22].

2.3. Cooling procedure

Since the energy $E(\boldsymbol{\sigma})$ of the metastable configurations depends only on the spin sequences $\boldsymbol{\sigma} = \{\sigma_i\}$ (cf equation (7)), it is sufficient to investigate the freezing behaviour of the Ising spins to determine e_{res} for the chain. The residual energy is then given by

$$e_{\mathrm{res}} = \lim_{N\to\infty} \lim_{t\to\infty} \frac{1}{N} [E(\{\sigma_i(t)\}) - E_0] \tag{15}$$

where

$$\sigma_i(t) = \sigma(x_i(t)) \equiv \operatorname{sgn}(x_i(t) - c). \tag{16}$$

Since the ground state is periodic [17] its energy E_0 can be calculated easily from (7).

Assuming the system to be self-averaging, e_{res} can be written as follows:

$$e_{\text{res}} = \lim_{N\to\infty} \lim_{t\to\infty} \frac{1}{N} [\langle E\rangle(t) - E_0] \tag{17}$$

where

$$\langle E\rangle(t) = \sum_{\boldsymbol{\sigma}} E(\boldsymbol{\sigma}) p(\boldsymbol{\sigma}, t). \tag{18}$$

In order to calculate $\langle E\rangle(t)$, the magnetization $\langle \sigma_n\rangle(t)$ and the correlation functions $\langle \sigma_n \sigma_m\rangle(t)$ must be known. These quantities can be determined from the solution of

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \sigma_{n_1}\sigma_{n_2}\ldots\sigma_{n_\nu}\rangle = -2\sum_{\mu=1}^{\nu}\langle \sigma_{n_1}\sigma_{n_2}\ldots\sigma_{n_\mu}w_{n_\mu}(\boldsymbol{\sigma}, T(t))\rangle \qquad \nu = 1, 2, \ldots \tag{19}$$

with the corresponding equilibrium values as initial conditions [22]. This system in general gives rise to a hierarchy of *coupled* equations with *time-dependent* coefficients due to the time-dependent temperature. Its solution for the rates $w_n(\boldsymbol{\sigma})$ given by (12) or (13) is not known except for $\delta = 0$.

Analytically the cooling process will be described by a time-dependent temperature $T(t)$ determined by:

$$\dot{T} = -\gamma f(T(t)) \tag{20}$$

where γ is the cooling rate and $f(T)$ specifies the cooling scheme [19]. As we will see from the simulations, it is $f(t) \simeq T$ in our case. However, it has been shown that the residual energy is independent for a large class of functions f [12, 19].

To determine $E(\{\sigma_i(t)\})$ in (15) we numerically integrated the equations of motion

$$m\ddot{x}_i + \gamma\dot{x}_i + \frac{\partial V}{\partial x_i} = 0 \tag{21}$$

where m is the mass of a particle. Due to the frictional term the energy of the system decreases. The vibrational degrees of freedom can be regarded as a heat bath coupled to the Ising spins and by means of the decreasing vibrational energy the friction simulates a cooling procedure for the spins.

We now give the relevant details of the molecular dynamics method used to integrate (21). Introducing scaled variables, we can set $C_1 = m = 1$ which leads a typical time scale of order 2π time units for the oscillation time of a particle in its on-site potential. The numerical algorithm we applied to solve the differential equations has been described elsewhere [18]. As step size we used $\Delta t = 0.025$ time units. This value is larger than the one used in [18], because the accuracy of the integration algorithm is not so critical for the kind of questions studied here. The initial conditions in phase space were chosen such that the energy per particle was well above the highest barrier for single spin flips, thus allowing the system to move in phase space unhindered by the potential barriers. Equilibrium was achieved after about a few hundred time units (see also [18]). The system size was $N = 5000$ particles and sometimes $N = 15\,000$ to check for finite-size effects. A cooling run was performed long enough to assure that the configurational degrees of freedom have become frozen, i.e. that the final temperature was much less than $B_{\min}$, the minimum barrier height.

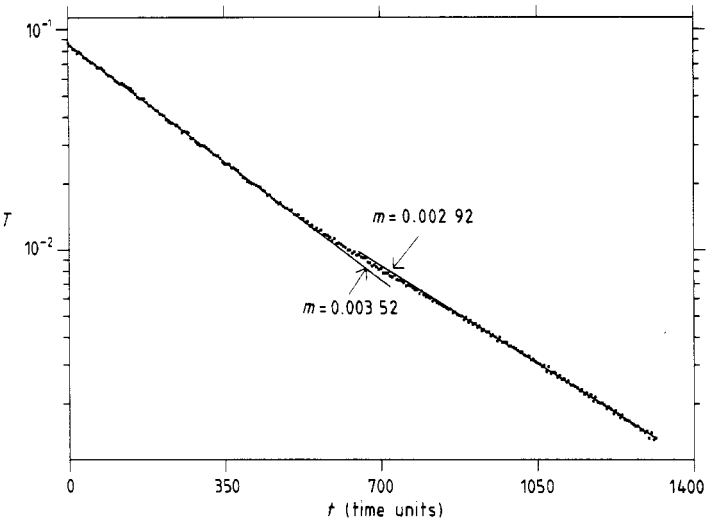


Figure 1. Time dependence of the temperature for a damping constant $\gamma = 0.003$. Parameters: $a_+ = 5.0$, $a_- = 0.2$, $b = 11.7$, $c = 4.6$, $C_2 = -0.08$, $\eta = 0.096$ and $h = 0$.

The effect of this cooling scheme is shown in figure 1, which depicts the temperature T (defined via the kinetic energy) as a function of time for a small damping constant. The two straight lines are exponentials fitted to the data. It is clear that, except for a short intermediate time range, $T(t)$ is well represented by an exponential decline. For short times the decay rate seems to be a bit larger than γ and for long times it is very near to γ. The latter observation is easily understood since for large times the configurational degrees of freedom are frozen and the vibrational part behaves *purely* harmonically. Note that the short intermediate time range, where $T(t)$ does not decrease exponentially, is the time range where the system freezes.

To get a feeling for the magnitude of the temperatures and cooling rates considered here, we can assume the following values for the parameters of the potential energy: unit of length = 1 Å, force constant $C_1 = 0.65\ \mathrm{kg\,s^{-2}}$, mass $m = 16$ u. At high temperatures (with respect to $B_{\max}$, the maximum barrier height for single spin flips) the particle had a RMS velocity of about 0.3 length × time^{-1} yielding a temperature of about 45 K. $B_{\max}$, which depends on η, is about 15-25 K. The lowest cooling rate γ has been 1.5×10^{-5} time units^{-1} which correspond to about $10^9\ \mathrm{K\,s^{-1}}$.

3. Results

The parameters of the potential energy (4) can be chosen such that the magnetic field h in (7) is zero. Since the dynamical behaviour of the chain for $h = 0$ differs very strongly from that for $h \neq 0$, the two cases will be treated separately. For all simulations we chose $\eta > 0$.

3.1. $h = 0$

Although the transition rates (13) are rather simple in this case, the set of differential equations (19) is still coupled. The only known example for which the hierarchy gets

decoupled and solvable is $\delta = 0$ [22, 23]. Reiss has solved this case even in the presence of an arbitrary time-dependent temperature [24]. His result gives $\langle \sigma_m \sigma_n \rangle(t)$ in terms of integrals involving $T(t)$. Using this result one of us (RS) computed $e_{\text{res}}(\gamma)$ for a *slow* quench and an attempt frequency of the form $\alpha(T) = \alpha_0 \exp(-\beta B)$ [19]. $e_{\text{res}}(\gamma)$ was found to exhibit a power law with an exponent

$$\frac{2J}{B+4J}. \tag{22}$$

If we insert the transition rates from (13) into the coupled equations of motion for the correlation functions, an approximate solution can be obtained if we replace $\langle \sigma_m \sigma_{n-1} \sigma_n \sigma_{n+1} \rangle(t)$ $(m \neq n)$ by $\langle \sigma_m \sigma_n \rangle(t)$. This approximation is exact for the equilibrium. The resulting differential equations for $\langle \sigma_m \sigma_n \rangle$ are identical with those for $\delta = 0$ considered in [19]. Therefore we obtain again a power law for $e_{\text{res}}(\gamma)$. The exponent follows from (22) with $B = |J_0|(1-4\eta)$ and $J = 2\eta|J_0|$. This barrier height B is just $B_{\min}$ up to order η. For the exponent we thus find

$$\mu = \frac{4\eta}{1+4\eta}. \tag{23}$$

Another method for determining μ has recently been introduced by Stinchcombe *et al* [20]. This approach is based on more physical considerations and exploits an idea proposed by Cordery *et al* for calculating critical dynamical exponents [25]. The idea of Stinchcombe *et al* is as follows. For small cooling rates the system will fall out of equilibrium at a rather low temperature T_f. At low temperatures the predominant spin configurations consist of large domains of spins with equal sign separated by domain walls. The relaxation time $\tau(T_f)$ is now related to the diffusive motion of the walls. The mean distance between two walls is $\xi(T_f)$, the correlation length. If $\Gamma(T_f)$ denotes the rate for wall diffusion, then $\tau(T_f)$ is the mean time for a wall to move a distance $\xi(T_f)$ (measured in lattice constants) which is:

$$\tau(T_f) = \frac{\xi(T_f)^2}{\Gamma(T_f)}. \tag{24}$$

It is reasonable to assume that the system falls out of equilibrium at that temperature T_f for which (see [3, 19])

$$\tau(T_f) = \gamma^{-1}. \tag{25}$$

Equations (24) and (25) allow one to determine $T_f(\gamma)$. For the most general Ising model with bilinear and ferromagnetic interactions the residual energy is given by

$$e_{\text{res}} = \sum_{n>0} J_n \Delta_n(T_f) \qquad \Delta_n = 1 - \langle \sigma_i \sigma_{i+n} \rangle \ll 1 \tag{26}$$

where J_n is the nth nearest-neighbour coupling constant. Substituting T_f into this expression we obtain $e_{\text{res}}(\gamma)$.

Let us now apply this method to the original transition rates given by (13). Because for low temperatures the creation rate for pairs of walls is much smaller compared to the flip rate within a wall, it is the latter which determines Γ (cf also [25]). The corresponding barrier height for moving the wall by one lattice constant is (use (6), (8) and A, B, J_0 from [17])

$$B = |J_0| + O(\eta^{\xi(T_f)}) \tag{27}$$

leading to

$$\Gamma(T_f) \simeq \alpha_0 \exp(-\beta_f |J_0|). \tag{28}$$

The correlation length is given by

$$\xi(T_f) \sim \frac{1}{\Delta_1(T_f)}. \tag{29}$$

It is not difficult to show that for an Ising model with coupling constants $J_n > 0$ $(n = 1, \ldots, r)$ which decrease rapidly enough, Δ_1 is given at sufficiently low temperatures by

$$\Delta_1(T_f) \sim \exp\left(-2\beta_f \sum_{n=1}^{r} nJ_n\right). \tag{30}$$

From (24), (25), (28)-(31) we find that

$$\beta_f \sim \frac{-\ln \gamma}{|J_0| + 4\sum_n nJ_n}. \tag{31}$$

Since we have $J_n = 2|J_0|\eta^n > 0$, the residual energy is given by

$$e_{res} = 2|J_0| \sum_n \eta^n \Delta_n \tag{32}$$

which in leading order of Δ_1 reduces to

$$e_{res} \sim \Delta_1(T_f) \tag{33}$$

because $\Delta_n \sim n\Delta_1$ for low temperatures. Substituting $\Delta_1(T_f)$ and $T_f(\gamma)$ into (33), we get finally the power law†

$$e_{res} \sim \gamma^{\mu} \qquad \text{with} \qquad \mu = \frac{4\eta}{(1+\eta)^2 + 4\eta}. \tag{34}$$

Note that this result coincides with the result (23) in leading order of η and that for this result to hold T_f must be so small that the domains are much larger than a lattice constant, which requires

$$\exp(4\beta_f |J_0| \eta) \gg 1 \qquad \eta > 0. \tag{35}$$

This condition leads to

$$\frac{k_B T_f}{|J_0|} \ll 4\eta. \tag{36}$$

Since $k_B T_f / |J_0| \sim -1/\ln \gamma$ (cf equation (31)) we find an upper bound

$$\gamma_c = A \exp\left(-\frac{1}{4\eta}\right) \qquad A = O(1) \tag{37}$$

such that (35) is guaranteed for $\gamma \ll \gamma_c$, which in turn implies that the power law holds. For given γ the CPU time needed to do a cooling run is $O(\gamma^{-1})$. Therefore, and because of (37) the asymptotic regime, where $e_{res} \sim \gamma^{\mu}$, cannot be reached for very small η.

† Note that we neglect a term of order $\eta^{\xi(T_f)}$ which becomes arbitrarily small for γ small.

Figure 2 illustrates this behaviour for a system of 400 particles. It shows the evolution of the pseudospins during a cooling run for two different η values but for the same cooling rate ($\gamma = 0.000\,33$). For $\eta \simeq 0.277$ (figure 2(a)) large domains are found at the end of the run, whereas for $\eta \simeq 0.034$ (figure 2(b)) the domains in the final stage are much smaller.

To determine $e_{res}(\gamma)$ numerically we usually carried out the simulation for six different initial configurations in phase space for $3.3 \times 10^{-3} \leq \gamma \leq 10$ and for three initial configurations for $\gamma < 3.3 \times 10^{-3}$. The resulting residual energies scattered a little (for fixed γ) but tests showed that the width of this scattering decreases if the size of the system was increased [21]. Thus $e_{res}(\gamma)$ seems to become a sharp quantity in the thermodynamic limit. Figure 3 depicts $e_{res}(\gamma)$ for various initial configurations and shows the scattering of the data. Figure 4 shows $e_{res}(\gamma)$, averaged over the different initial configurations, for different η.

It is clear from these figures that the global behaviour of $e_{res}(\gamma)$ does not depend on η very strongly. For large γ the function saturates because the system relaxes to a metastable configuration very near to its initial configuration. If we decrease γ, $e_{res}(\gamma)$ begins to decay and shows some plateaux. The explanation for these is given below. For still smaller γ, $e_{res}(\gamma)$ turns over into an asymptotic behaviour which can be fitted by a power law (straight lines). Note that the range over which this fit is reasonable

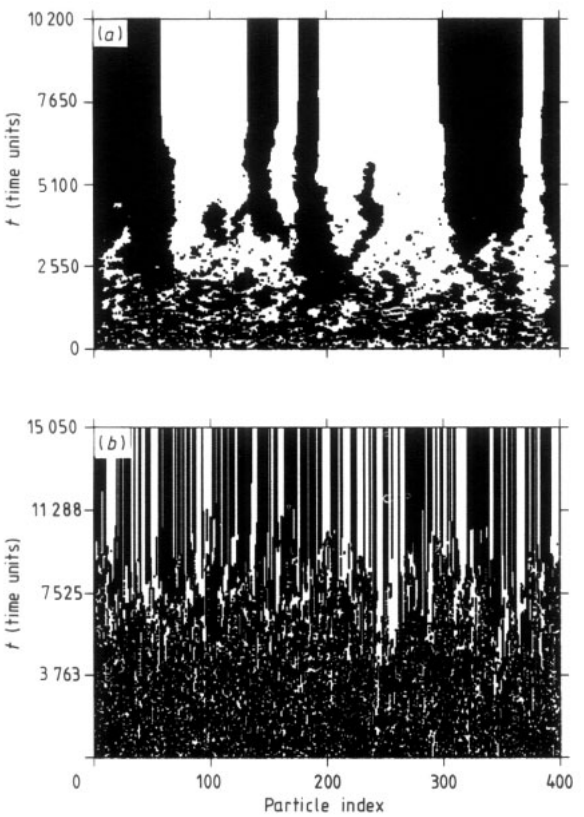


Figure 2. Spin configurations as a function of time for two different cooling runs with $\gamma = 0.000\,33$. Parameters: $a_+ = 5.0$, $a_- = 0.2$, $b = 11.7$, $h = 0$. (a) $c \simeq 3.194$, $C_2 = -0.17$, $\eta \simeq 0.277$. (b) $c \simeq 4.875$, $C_2 = -0.032$, $\eta \simeq 0.034$.

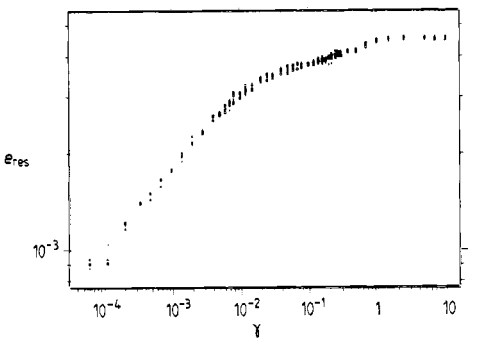
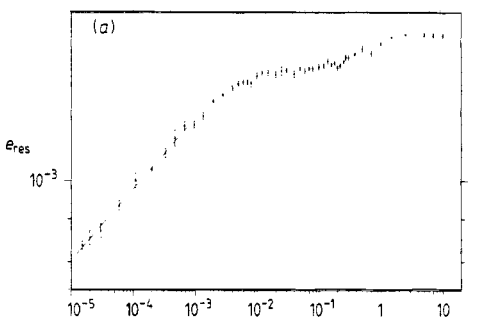
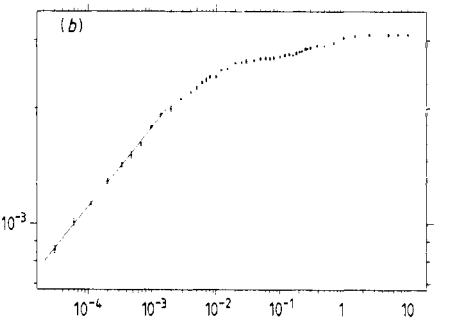
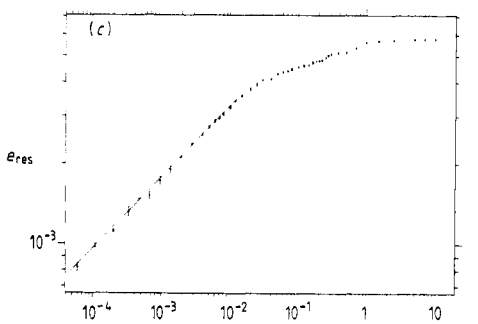
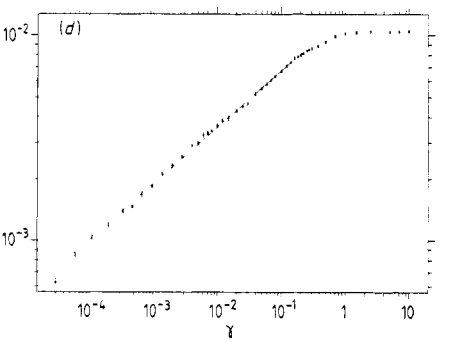


Figure 3. Residual energy as a function of cooling rate. Different symbols correspond to different initial conditions. Parameters as in figure 1.









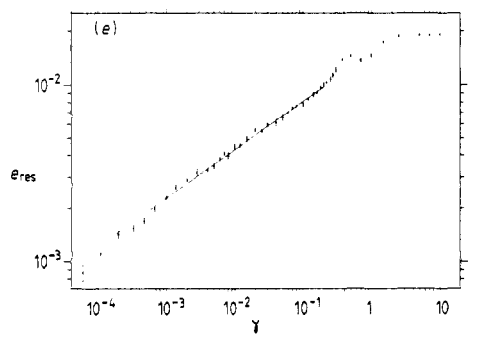


Figure 4. Residual energy, averaged over several initial conditions, for different η and $h = 0$. The straight lines represent the best power-law fit. Parameters: $a_+ = 5.0$, $a_- = 0.2$, $b = 11.7$, C_2: variable, c: such that $h = 0$. The η values chosen are: (*a*) $\eta = 0.034$, (*b*) $\eta = 0.068$, (*c*) $\eta = 0.117$, (*d*) $\eta = 0.202$, (*e*) $\eta = 0.277$.

decreases with decreasing η. This is due to the fact mentioned above that the cross-over to the power-law behaviour shifts to smaller values of γ if η decreases (cf equation (37)). Therefore the result for μ may be affected by a significant *systematic* error (of unknown size) for small η, since we are not entirely sure that the asymptotic regime has already been reached. The numerical values for μ, its error and the analytical value from (34) are given in table 1. Figure 5 shows the η dependence of μ. For $0.048 \leqslant \eta \leqslant 0.135$ the deviation between the analytical and numerical result are quite small, i.e. less than 6%, whereas for $\eta \simeq 0.034$ and $\eta \geqslant 0.20$ it is about 30%. The discrepancy for the smallest η value probably originates from not having reached the asymptotic regime yet. For larger η we have found that the temperature $T_f(\gamma)$ at which the system freezes is comparable to or larger than B_{min}, even for the smallest γ values (note that B_{min} vanishes for $\eta \to \frac{1}{3}$). Thus the Markov assumption leading to (10) might no longer be justified, and in addition the transition rates (13) could also be incorrect for this case.

Although the numerical calculation can also be performed for $\eta > \frac{1}{3}$, (which was done for $\eta \simeq 0.666$, where a power law with $\mu \simeq 0.40$ was found) the analytical treatment is now more difficult because the one-to-one correspondence between metastable configurations and spin sequences no longer holds.

We have also plotted e_{res} as a function of $\ln(-\ln \gamma)$ (figure 6). This graph rules out a logarithmic dependence of e_{res} on γ as proposed by Huse and Fisher [12].

Table 1. Exponent μ_{num}, statistical error $\Delta\mu_{num}$ (from the numerical simulation) and exponent μ_{theo} (from equation (34)) for different η and $h = 0$.

η	μ_{num}	$\Delta\mu_{num}$	μ_{theo}
0.034 22	0.0853	0.0032	0.1135
0.048 35	0.1473	0.0012	0.1496
0.068 50	0.2051	0.0032	0.1935
0.096 12	0.2467	0.0016	0.2424
0.117 35	0.2666	0.0016	0.2732
0.135 35	0.2869	0.0008	0.2958
0.202 41	0.2742	0.0013	0.3590
0.277 40	0.2737	0.0019	0.4048

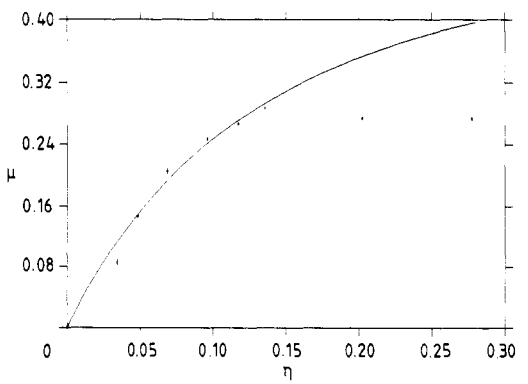


Figure 5. Exponent μ as a function of η. The error bars show only the statistical errors of the fits, systematic errors may be larger. The solid curve represents the theoretical values from (34). Parameters as in figure 4.

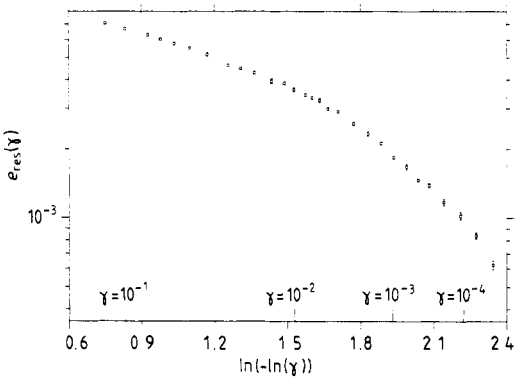


Figure 6. ln e_{res} as a function of ln($-\ln\gamma$). Parameters as in figure 4. Compare also figure 4(d). η is chosen to be $\eta = 0.202$.

Let us finally come back to the plateaux found in $e_{res}(\gamma)$ for γ not too small. Here we will give only some rather qualitative arguments to explain these features. More detailed calculations can be found in [21]. To understand this phenomenon one has to know that for such large damping ($\gamma \approx 0.2$) the particles oscillate only a few times in their *local* double well potential, crossing the point $x = c$ only once or twice before they settle into one of the two wells. Take for simplicity an ensemble of non-interacting particles moving in an *asymmetric* double well potential. The distribution of the positions and velocities should be given by the Gibbs distribution with a temperature which is not too large compared with the barrier height. Thus the distribution is peaked around both local minima. Therefore, and because of the asymmetry, the RMS velocity is less for those particles moving in the upper well than those moving in the lower one. Due to the velocity-dependent friction, the energy dissipation is less for those particles with the lower velocity. For strong damping (i.e. $\gamma > 1$) all particles stay in their initial well. If γ is decreased (e.g. $\gamma \simeq 1$) some of the particles will move from the upper well to the lower one and fewer will move from the lower well to the upper one, because these particles lose their energy faster as they have a larger velocity. Thus there is a net flow from the upper to the lower well and e_{res} decreases. If γ is decreased further, a significant part of the particles from the lower well can overcome the barrier now and will be trapped in the upper well. This flow can compensate or even overcompensate the flow from the upper to the lower well. Hence $e_{res}(\gamma)$ will exhibit a plateau or may even be increasing in a certain range of γ.

If there is a hierarchy of local double well potentials, it may be possible that many different plateaux occur, as the location of a plateau depends on the parameters of the double well potential. We have not investigated this point in more detail. From the arguments just presented, we would expect such plateaux to occur in the case $h \neq 0$ as well, as we will indeed see in the next section.

3.2. $h \neq 0$

In the following we will restrict ourselves to $h > 0$. Similar results are expected for $h < 0$.

The analytical calculations in this case are much more complicated than those for $h = 0$ due to the rather complex transition rates (cf equation (12)). Therefore we content ourselves with a very simple approximation for the analytical calculation of $e_{res}(\gamma)$.

Using the transition rates (12), the differential equation (19) for $\langle\sigma_i\rangle(t)$ involves, besides $\langle\sigma_i\rangle$, also $\langle\sigma_i\sigma_{i+n}\rangle$ for $n=1$, 2 and $\langle\sigma_{i-1}\sigma_i\sigma_{i+1}\rangle$. Assuming $\beta h \gg 1$, we perform the simplest possible decoupling:

$$\langle\sigma_i\sigma_{i+n}\rangle \simeq \langle\sigma_i\rangle^2 \simeq 1-2\varepsilon \tag{38a}$$

$$\langle\sigma_{i-1}\sigma_i\sigma_{i+1}\rangle \simeq \langle\sigma_i\rangle^3 \simeq 1-3\varepsilon \tag{38b}$$

where $\varepsilon = 1-\langle\sigma_i\rangle \ll 1$. Introducing this into the equation for $\langle\sigma_i\rangle(t)$ yields a *linear* differential equation for $\varepsilon(t)$ from which we find after a lengthy calculation (see [21]) the relaxation time

$$\tau(T) \simeq \alpha_0 \exp(\beta B) \tag{39}$$

where

$$B = \frac{1}{4|J_0|}[2|J_0|(1-2\eta)-h]^2 \tag{40}$$

is the barrier (up to order η) for flips $\ldots + - + \ldots \to \ldots + + + \ldots$. From the criterion (25) we get

$$\exp(-\beta_f) \sim \gamma^{1/B}. \tag{41}$$

On the other hand, we know from an analytical calculation that

$$\varepsilon(T_f) = 1-\langle\sigma_i\rangle(T_f) \sim \exp(-\beta_f\Delta) \tag{42}$$

with

$$\Delta = 8|J_0|\eta + 2h \tag{43}$$

the asymmetry (up to order η) between the configurations $\ldots + - + \ldots \to \ldots + + + \ldots$.

Taking into account only the nearest-neighbour interactions, we obtain from (7) and (17) for e_{res}:

$$e_{res} \simeq 2|J_0|\eta[1-\langle\sigma_i\sigma_{i+1}\rangle(T_f)] + h[1-\langle\sigma_i\rangle(T_f)] \tag{44}$$

which simplifies to

$$e_{res} \simeq (4|J_0|\eta + h)\varepsilon(T_f) \tag{45}$$

when (38) is used. From (41), (42) and (43) we find again a power law for $e_{res}(\gamma)$ with an exponent

$$\mu = \Delta/B. \tag{46}$$

This result agrees with that derived by Huse and Fisher for a *single* two-level system [12]. This is obvious since the mean-field approximation (38) reduces the problem to independent two-level systems.

We must keep in mind that this result holds only when the magnetization at T_f is *appreciable*, which is true for $\beta_f h \gg 1$. If $h \ll J$ ($J = 2|J_0|\eta$) there exists a range for γ such that $\beta_f(\gamma)h \ll 1$ but $\beta_f(\gamma)J \gg 1$. This means that the system will freeze in before a significant magnetization has been built up, but where large domains already exist. In this case the whole freezing process must be described in the same way we did for the case $h=0$ and therefore we find in this γ range a power law with an exponent which is given by (34). Only for γ values lying well below this γ range (i.e. where also $\beta_f h \gg 1$ holds) will we find a power law with an exponent given by (46).

This behaviour makes the numerical examination of a power law with μ given by (46) rather difficult. The discussion above suggests choosing h/J large. But in this case

we found that the *finite* chain relaxes to the ground state even for relatively large γ. On the other hand, for h/J small we will observe only the intermediate behaviour for $e_{res}(\gamma)$ given by (34). The asymptotic power law occurs at such small γ values that they cannot be treated numerically. Figure 7 presents the results for $e_{res}(\gamma)$ for $h>0$. For the small γ-range we have fitted a power law. The exponents are given in table 2. For $h/J \leqslant 0.5$ we found the final magnetization to be quite small and, as follows from table 2, the numerical exponent agrees quite well with $\mu_{theo} \simeq 0.218$ for $h=0$ and $\eta \simeq 0.0819$ (equation (34)).

For $0.5 < h/J < 0.9$ the correspondence between μ_{num} and μ_{theo} (equation (46)) seems to be fair and for $h/J > 0.9$ the ground state was almost reached even for γ

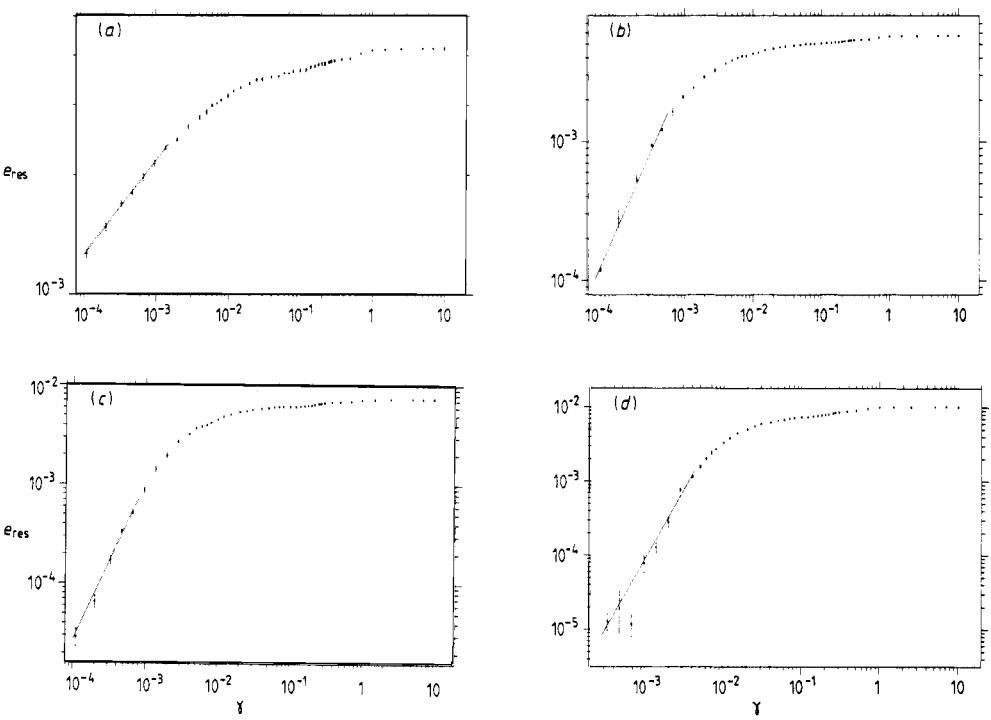


Figure 7. Residual energy $e_{res}(\gamma)$ for different $h/2\eta J_0$ and $\eta \simeq 0.0819$. Parameters: $a_+ = 5.009$, $a_- = 0.201$, $b = 11.698$, $C_2 = -0.07$, c: variable. Values chosen for $k/2\eta J_0$ are: (*a*) 0.100, (*b*) 0.532, (*c*) 0.996 and (*d*) 1.924.

Table 2. Exponent μ_{num}, statistical error $\Delta\mu_{num}$ and exponent μ_{theo} (from equation (46)) for different $h/2\eta J_0$ and $\eta = 0.0819$.

$h/2\eta J_0$	μ_{num}	$\Delta\mu_{num}$	μ_{theo}
0.009 96	0.240	0.0034	0.982
0.099 60	0.239	0.0071	1.045
0.326 29	0.988	0.082	1.216
0.532 37	1.134	0.016	1.389
0.996 05	1.592	0.083	1.856
1.923 41	1.877	0.073	3.350

values which were not very small. Thus no reasonable determination of the asymptotic behaviour could be made, and therefore no definitive conclusions can be drawn.

4. Summary and conclusions

We have studied the dependence of the residual energy e_{res} on the cooling rate γ for a chain of particles with *anharmonic* and *competing* interactions. This model does not contain any extrinsic disorder as most spin-glass models do. Nevertheless, its potential energy in configuration space exhibits a complex landscape. If the parameters of the model satisfy certain conditions all metastable states can be uniquely classified by Ising spin configurations. This correspondence has been used to describe the dynamics of the chain by a kinetic Ising model. Assuming a time-dependent temperature, we found a power law $e_{res} \sim \gamma^{\mu}$ for the residual energy of this kinetic model.

For *vanishing* magnetic field, $\mu(\eta)$ was determined analytically by means of a method proposed recently for computing $e_{res}(\gamma)$ for an Ising model with alternating nearest-neighbour interactions [20]. This method, which originally was introduced to compute the critical dynamical exponent z [25], also allows one to show that $\mu = z^{-1}$ [20].

Our simulations support these analytical calculations in that we also find a power law. The range of γ where this holds is between two and four orders of magnitude. This and the exclusion of a logarithmic dependence seems to confirm the power-law behaviour which we have found earlier [16]. Comparing the η dependence of μ derived from the kinetic Ising model (equation (34)) with that of our simulations, a satisfactory agreement for $\eta < 0.15$ is seen, whereas for $\eta > 0.15$ significant deviations of about 30% occur. This disagreement is not well understood. The numerical values of μ for large η seem to converge to an asymptotic value $\mu_0 \simeq 0.27$. A very similar value has also been found for a different set of parameters $a_{\pm}$ and b.

For *non-vanishing* magnetic field the results for e_{res} are less conclusive. Within a mean-field approximation we have found that the asymptotic behaviour of $e_{res}(\gamma)$ is determined by the freezing of a certain type of two-level systems. Again a power law follows for $e_{res}(\gamma)$ for which we also found evidence in our simulations. However, the analytically determined exponents agree with those determined numerically only for an intermediate range of h/J. This is probably due to finite-size effects when h/J is large, and to not having reached the asymptotic regime for h/J small.

Let us finally mention that there exist regions in γ, for both $h = 0$ and $h \neq 0$, where e_{res} is practically independent of γ, i.e. there exist plateaux. These were attributed to the motion of the particles within their local and asymmetric double well potential in the case of not too small damping.

In summary we can say that at least for $h = 0$ our numerical and analytical results confirm a power law for the residual energy and therefore support the conjecture by Grest *et al* [1]. The numerically obtained exponent was in satisfactory agreement with that derived from a kinetic Ising model, provided that $\eta < 0.15$.

Acknowledgments

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